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Impact of Urban and Industrial Emissions on Mesoscale Precipitation Quality

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16. ABSTRACT

Results from an "acid rain" field study around the city of Philadelphia are presented. The study involved the sampling of wet deposition at a network of 40 sites within a distance of 60 km from the Delaware river. Emphasis was placed on event-type rain sampling of frontal and primarily nonconvective storms which are responsible for most of the Northeast's wet deposition. For most storms, meteorological conditions contributed to a predominant southeasterly transport. Since most of the area's urban and industrial emissions occur along the Delaware river, the Pennsylvania sector of the network was identified as the downwind (target) region; the New Jersey sector was the upwind (control) region. Local emissions appear to impact the deposition of nitrate (NO_3^-) which may register increases greater than 200%. It appears that this impact grows with distance from the river suggesting peaks beyond the 60 km boundary of the network. Comparisons with estimates of NO_x emissions reveal that a substantial fraction may be deposited as NO_3^- on the mesoscale. The impact of local emissions on total sulfur is less striking; for some storms the sulfur excess is only in the form of dissolved SO_2. Storm-to-storm variabilities in meteorological conditions, emissions, and oxidant availabilities are probable causes of the variability in the magnitude of the local impact.

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The Impact of Urban and Industrial Emissions on Mesoscale Precipitation Quality

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Results from an acid rain field study around the city of Philadelphia are presented. The study involved the sampling of wet deposition at a network of 40 sites within a distance of 60 km from the Delaware River. Emphasis was placed on event-type rain sampling of frontal and primarily nonconvective storms which are responsible for most of the Northeast's wet deposition. For most storms, meteorological conditions contributed to a predominant southeasterly transport. Since most of the area's urban and industrial emissions occur along the Delaware River, the Pennsylvania sector of the network was identified as the downwind (target) region; the New Jersey sector was the upwind (control) region. Local emissions appear to impact the deposition of nitrate (NO_3^-) which may register increases greater than 200%. It appears that this impact grows with distance from the river suggesting peaks beyond the 60 km boundary of the network. Comparisons with estimates of NO_x emissions reveal that a substantial fraction may be deposited as NO_3^- on the mesoscale. The impact of local emissions on total sulfur is less striking; for some storms the sulfur excess is only in the form of dissolved SO_2. Storm-to-storm variabilities in meteorological conditions, emissions, and oxidant availabilities are probable causes of the variability in the magnitude of the local impact.

One of the serious uncertainties in the acid deposition problem is the role of large urban and industrial centers. The influence of emissions from these centers needs to be quantified; this would greatly enhance understanding of the source-receptor relationship and assist the development of effective mitigation strategies. Of particular interest is the situation in the northeastern United States and southeastern Canada where urban densities are high and where sensitive areas such as the Adirondack Mountains[1] are considered "target" regions of long range transport from midwestern power centers.[2]

In an earlier paper[3] we reported results from the exploratory phase of a field study of acid wet deposition around the city of Philadelphia. This research has been funded as part of the National Acid Precipitation Assessment Program[4] by the Environmental Protection Agency (EPA) and addresses the issue of urban source contributions to the total acid deposition budget within a ~60 km radius of the city. The study involves precipitation event sampling at a network of 40 sites and emphasis has been placed on frontal and primarily nonconvective storms. The rationale for this emphasis is that these storms are responsible for most of the wet deposition in the Northeast. Furthermore, a substantial data base of equivalent deposition for summer convective storms exists for the city of St. Louis.[5] The two sampled storms during the exploratory phase (November and December 1983) demonstrated similar meteorological features but remarkably different wetfall chemistry. The November storm showed a definite influence of the area's emissions on the deposition of several inorganic ionic species, most notably nitrate, while the December storm showed only an excess, above background, of dissolved SO_2 deposition in the downwind sector.[6] Several hypotheses explaining this contrast have been presented; they include emissions modulation (weekday-weekend effect), subtle meteorological differences in the boundary layer, and the availability of oxidants, particularly OH below clouds and H_2O_2 in-cloud. Both are considered responsible for rapid conversion of NO_2 and SO_2 to HNO_3 and H_2SO_4 respectively.

There is considerable uncertainty regarding the magnitude and extent of the impact of urban emissions. Only a limited number of studies have relied on extensive field measurements. The study at St. Louis[7] was confined to summer season convective storms and concluded that the measured excess, above background, of sulfate and nitrate were incorporated by scavenging of gaseous precursors. This implied rapid oxidation rates for oxides of sulfur and nitrogen in warm polluted environments. Bridgman[8] disputed this claim and suggested that primary emissions may be responsible for the excess sulfate with nucleation the major cause of sulfate scavenging. Uppsala, Sweden, has been the subject of several studies with some contradictory results. It is a moderately sized city (population approximately 100,000) and differs from similarly-sized cities typical of North America in that 65% of the SO_2 emitted in that city comes from a single district heating plant. Andersson[9] and Högström[10] measured a significant impact of the urban plume on downwind wet deposition; in particular, Högström estimated that two-thirds of the emitted sulfur was deposited within 50–100 km of the source, indicating rapid SO_2 to sulfate transformation. Rodhe,[11] on the other hand, concluded that less than 5% of the emitted sulfur was deposited in the near field; his conclusion, however, was based on limited analyses of fresh snow samples over a 12-day period.

Other studies on the deposition of urban plumes include work by Benarie,[12] Davies,[13] Shaw,[14] and Dasch and Cadle.[15] These studies, however, did not involve extensive networks and, consequently, their results have greater uncertainties. Benarie and Shaw concluded that local sources had significant

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Table I. Summary of important meteorological features of the sampled storms.

Storm[a]	Period	Precipitation type	Precipitation characteristics	Weather system
1111	1230 EST 11/10/83 to 2200 EST 11/10/83	Rain, steady and stable	Fairly uniform spatially, heavier in NJ, average approx. 3.4 cm.	Overrunning a high in New England. Low pressure system moving up the coast.
1204	0300 EST 12/4/83 to 1000 EST 12/4/83	Rain, steady and stable	Uniform spatially, slightly heavier in NJ, average approx. 3.3 cm.	Overrunning a high in New England. Low pressure system moving up the coast.
0306	0530 EST 3/5/84 to 0300 EST 3/6/84	Started as snow, stable, continuous	Spatially uniform, average amount ~2 cm.	Overrunning an advancing W-E warm from the south.
0314	0400 EST 3/13/84 to 0000 EST 3/14/84	Started as snow, stable, continuous	Fairly uniform spatially, heavier in NJ, average ~4.3 cm.	Overrunning a cold high in New England. Formation of secondary low.
0321	0700 EST 3/21/84 to 1600 EST 3/21/84	Rain, convective, intermittent showers	Nonuniform spatially, average in NJ ~0.3 cm, average in PA ~0.8 cm.	Overrunning an advancing W-E warm front from the south.
0326	0700 EST 3/25/84 to 0000 EST 3/26/84	Rain, light but steady, stable	Nonuniform spatially, average in NJ ~1.7 cm, average in PA ~0.3 cm.	Low pressure system moved out to sea, south of network.
0329	2000 EST 3/27/84 to 2000 EST 3/29/84	Light rain initially then heavy, some snow to light rain stable with imbedded convection	Spatially uniform, average ~5.7 cm.	Deep low formed in the southeast. Tracked to the northeast, moved out to sea off the NJ coast.
0405	0830 EST 4/4/84 to 1100 EST 4/5/84	Rain, fairly steady, stable	Fairly uniform spatially, average ~5.8 cm.	Overrunning a warm W-E warm front attached to low which passed just west of network.
0414	1500 EST 4/13/84 to 0300 EST 4/14/84	Light rain, convective, intermittent showers	Nonuniform spatially, more in PA, average ~0.3 cm.	Weak warm front passage and advancing second W-E warm front.
0415	0100 EST 4/15/84 to 1200 EST 4/15/84	Light rain, convective, intermittent showers, thundershower	Nonuniform spatially, more in NJ, average ~0.5 cm.	Advancing W-E warm front from the south (see above).
0424	2030 EST 4/22/84 to 1800 EST 4/23/84	Rain, fairly steady, stable	Fairly uniform spatially, more in NJ, average ~1.3 cm.	Secondary low pressure system off Virginia coast moving northward.

[a] Each storm is identified by a four digit number indicating the date of sample collection, i.e., for 1111 samples were collected on the 11th of November.

impact on near field deposition around Paris, France and Halifax, Canada, respectively; Dasch and Cadle found no effect of urban emissions of Detroit, Michigan on the precipitation chemistry of a nearby site.

This paper presents results from the main field effort which was conducted during March and April of 1984. The results complement the preliminary study,[3] permit an enhanced perspective on urban-scale wet deposition, and promote a substantive evaluation of the influence of urban emissions on precipitation quality.

Field Study

Sampling during the main field effort was conducted with a combination of automatic and manual collectors. Twenty-four of the 40 sites were instrumented with automatic wetfall collectors of the HASL (Health and Safety Laboratory) type, operating on the wet-only mode, and recording weighing bucket raingages geared for daily recording. Collection at the automatic samplers (*A*) was accomplished with two 1000 mL polyethylene bottles (of rectangular cross section) fitted with 10.1 cm diameter funnels welded to the caps. This arrangement minimized evaporation, contamination, and dissolved gas escape, and as two such bottle-funnel combinations fit in the standard 13-L bucket, quality control was enhanced. Interspersed among the *A* sites were 16 sites employing bulk precipitation samplers (*B*). The *B* collector was a simple 2-m pole on which a 1000-mL polyethylene bottle (with circular cross section) was attached. The bottle was fitted with a 11.5-cm diameter funnel as with the *A* sampler. *B* samplers were deployed when rain was forecast and collected as soon after the termination of rainfall as possible; they were, therefore, exposed to a period of dryfall. Apart from increasing the sampling density, *B* samples also provided a measure of this dryfall contamination, which is useful in assessing the quality assurance of event-type sampling. Recording raingages were also installed at select *B* sites and several *B* collectors were deployed at various *A* sites for comparison purposes. Further details of the experimental procedures can be found in Patrinos and Brown,[3] Dana *et al.*[16] and Patrinos *et al.*[17] Precipitation samples were rapidly transported to a field laboratory where they were weighed and aliquots were taken for pH, conductivity, and dissolved SO_2 measurements. It is important to emphasize that a rigorous quality assurance (QA) program was developed for this study;[18] this included a series of field blanks from two laboratories [Brookhaven National Laboratory (BNL) and Battelle Pacific Northwest Laboratory (PNL)], blind duplicate chemical analyses at these laboratories and a variety of field checks.

Following the field effort the procedure was to reconstruct the important meteorological features of each storm in order to compare the wet deposition in areas least affected by urban emissions (control region) to the wet deposition in areas most affected by the urban emissions (target region). The bulk of the data used in these reconstructions were acquired by the National Weather Service (NWS) at its regular stations. These included information from the radiosonde flights at Atlantic City and occasionally from Wallops Island (Virginia) and Washington-Dulles (Maryland) and the 850 mb level winds. Additional data were provided from the installed network of recording raingages, the acquisition of sequential color photographs of the Atlantic City and Harrisburg weather radars during storms, and support meteorological observations from local air quality agencies and local power plant meteorological towers such as the one at the Limerick Nuclear Generating Station, north of Philadelphia. Air quality data were provided by the responsible agencies of the city of Philadelphia and the states of New Jersey and Pennsylvania.

The Sampled Storms

A total of nine precipitation events were sampled during the two month experimental period. With two exceptions these events represent the period's total wet deposition. The exceptions are a snowstorm on March 8 and a number of convective showers which occurred during the early part of the week of April 16. The network was not activated during those times because of sampling problems associated with entirely frozen precipitation and because the showers were forecast as too scattered. Table I presents a summary of the important meteorological features of the sampled storms. This table includes the November 1983 storm (labeled 1111) and the December 1983 storm (labeled 1204) which were mentioned in the introduction. The majority of the storms were primarily nonconvective in nature and were associated with overrunning. This is typical of the dominant type of precipitation in the Northeast for this period: strong cyclonic systems forming in the southeastern United States and traveling to the northeast. A frequent occurrence was the development of a secondary low pressure system off the coast of Virginia which tracked to the north; this was particularly the case when the main cyclonic system was located further inland. This may be one of the reasons for the predominant southeast-northwest transport configuration during the precipitation events, as will be discussed later.

Detailed results from six of the 1984 sampled storms will be presented. Four of those storms were considered the "best" for sampling purposes for the following reasons: clear start and end in precipitation, fairly uniform (spatially) and sufficient amounts and satisfactory QA instrument performance. The other two storms are examples of less than ideal sampling conditions. The remaining three storms provide limited information on the impact of urban emissions: 0321 and 0326 had very low rainfall amounts on the New Jersey and Pennsylvania sectors respectively while 0329 was characterized by poor QA instrument performance because of destructive winds and a long period of precipitation. This was the intense coastal storm of March 27 to 29 which resulted in widespread instrument malfunctions (power losses, tipped sampling buckets, contaminated samples, etc.) and a limited number of valid data.

Storm 0306

The first storm of the sampling period started as snow but quickly changed to rain after three hours. The warm front crossed the network during the precipitation period and a secondary low pressure system formed over New Jersey. The passage of the front together with the proximity of the secondary low pressure system contributed to strongly veering

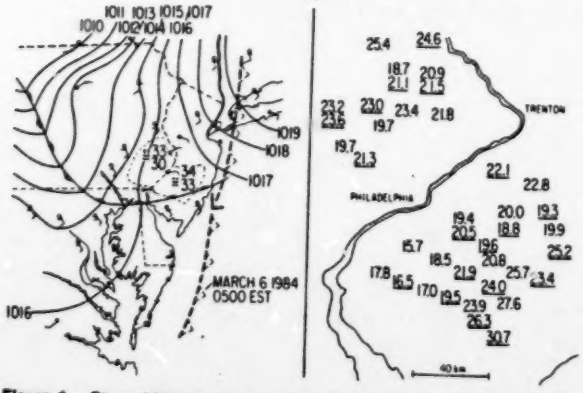

Figure 1. Storm 0306. Surface weather map for March 5, 1984, 1300 EST showing the secondary low 16 hours later. Also shown is the distribution of rainfall amounts (in mm) of storm 0306. The underlined values depict *B* collectors.

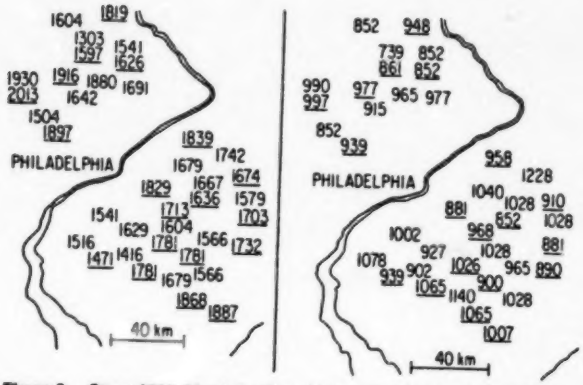

Figure 2. Storm 0306 (March 5 and 6, 1984). Left: the deposition of H^+ (from field pH). Right: the deposition of NO_3^-. Units are $\mu mol/m^2$. Underlined values depict *B* collectors.

transport during the precipitation event. Transport in this case is defined as the direction of the winds in the first few vertical kilometers; these winds will carry most of the locally emitted material which may be injected into the clouds or become available for below cloud scavenging. It is in this context that a control (upwind)-target (downwind) configuration is derived for each storm to effectively estimate the city's effect. Most of the emitted nitrogen and sulfur oxides in the sampling area originate along the Delaware Valley.[3] The inherent complexity (three-dimensionality) of the cyclonic storm system, particularly at higher levels, is assumed to affect both regions (control and target) equally, providing what may be considered the "regional" background in terms of deposited material. Thus, in order to detect the impact of urban emissions on the mesoscale it may be sufficient to develop a simplified model of the overall storm system based upon lower level flows (up to 5000 ft). Along with the sources of data mentioned earlier, use was made of the "Norwegian" model of a cyclonic storm.[19]

For 0306, based primarily on radiosonde data, it was determined that transport veered from easterly through southerly to westerly during the sampling period; there were, therefore, no obvious control and target regions for this storm. Figure 1 shows a representative surface weather map during the storm and the distribution of collected rainfall in the sampling bottles. The units of collected rainfall are in L/m^2 as deposition in order to standardize the differences in funnel sizes between the *A* and *B* collectors (diameters 10.1 cm and 11.5 cm, respectively); this unit is, of course, the commonly used mm of rain. The wetfall chemistry data will also be presented in deposition units ($\mu mol/m^2$) rather than concentration units ($\mu mol/L$) for two reasons. First, deposition data are applicable as inputs to most damage functions in assessment studies (e.g., for materials, forest or lake ecosystems, etc.). Second, the deposition unit incorporates the effect of dilution which occurs primarily during frontal, widespread and primarily nonconvective precipitation; ionic concentration of most species usually varies inversely with rainfall volume when the same air mass is involved. Concentration values may be computed from deposition values by dividing with the collected volumes and multiplying with the area surface of the funnel $\pi d^2/4$ (d = 10.1 cm for *A* collectors and d = 11.5 cm for *B* collectors). For reference purposes several ranges of concentration values will be given. The *A* values represent the average of the two bottles in each *A* collector. Both *A* and *B* values are compared against collocated or proximate raingage values to detect possible discrepancies. As seen in Figure 1, amounts were generally uniform with somewhat lower values to the southwest. *B* deposition values (underlined) are generally slightly larger than *A* values because the automatic collectors may miss the first few drops of the rain and may

Table II. Statistical summary of deposition data. The depicted three numbers per entry a-b-c are a = number of sites, b = mean, c = standard deviation. The units are mm for rainfall volume and μmol/m² for chemical species.

Storm		V[a]	H_F^{+b}	H_L^{+c}	NO_3^-	$So_4^=$	NH_4^+	Na^+	Cl^-	Ca^{++}
1111	B(NJ)	25-41.4-7.2	24-732-120	24-860-143	24-233-41	24-346-80	24-171-24	24-275-112	24-378-157	24-49-9
	B(PA)	13-23.6-4.1	13-1189-240	13-1331-281	13-716-153	13-492-89	13-285-117	13-92-18	13-146-30	13-35-15
1204	B(NJ)	25-35.2-3.5	25-823-70	25-908-74	25-285-28	25-305-58	25-85-17	25-562-393	25-633-412	25-47-4
	B(PA)	14-29.8-1.5	14-753-61	14-867-76	11-237-25	14-298-116	14-122-67	14-93-46	14-154-46	14-40-2
0306	A(NJ)	12-20.8-3.6	12-1599-88	12-1939-135	12-1032-88	12-766-61	12-622-76	12-162-35	12-202-28	12-54-11
	A(PA)	8-21.6-2.3	8-1637-203	8-2119-377	8-893-85	8-759-117	8-584-118	8-69-20	8-139-38	8-44-19
	B(NJ)	13-22.2-3.8	13-1745-112	13-1618-166	13-949-73	13-826-63	13-496-54	13-173-51	13-216-39	13-66-15
	B(PA)	6-22.5-1.5	6-1812-167	6-1759-278	6-929-60	6-839-112	6-472-46	6-68-22	6-145-39	6-65-23
0314	A(NJ)	9-47.6-7.0	9-761-102	9-1049-143	9-212-53	9-365-54	9-114-31	9-221-79	9-263-89	9-184-58
	A(PA)	10-39.6-8.3	10-846-102	10-1241-145	10-306-60	10-439-60	10-91-39	10-66-29	10-109-35	10-209-130
	B(NJ)	12-52.1-6.9	12-742-92	12-1294-159	12-255-48	12-496-82	12-168-39	12-313-137	12-346-150	12-279-62
	B(PA)	2-38.4-12.8	2-774-82	2-1505-47	2-348-55	2-552-96	2-189-116	2-194-136	2-194-109	2-677-247
0405	A(NJ)	12-52-6.8	12-1548-316	11-1951-406	12-313-51	12-1019-174	12-313-43	12-1910-528	12-2221-546	12-85-16
	A(PA)	11-70.2-10.3	11-2454-345	9-2969-383	10-906-142	10-1351-168	10-553-179	10-1053-302	10-1236-570	10-118-19
PNL[d]	B(NJ)	12-52.5-6.7	12-1528-334	9-2017-322	9-316-55	9-1087-212	9-322-36	9-2035-537	9-2155-565	9-91-15
	B(PA)									
	A(NJ)			e	12-313-63	12-919-211	12-370-55	12-1966-593	12-1920-687	12-48-9
	A(PA)			e	11-907-170	11-1291-207	11-660-203	11-1244-546	11-1376-530	11-71-14
BNL[d]	B(NJ)			e	12-337-118	12-947-232	12-350-115	12-1894-672	12-2115-781	12-46-6
	B(PA)									
0424	A(NJ)	11-15.2-3.3	11-333-61	e	11-107-36	11-135-34	11-60-14	11-86-50	11-170-79	11-20-4
	A(PA)	9-11.8-1.4	9-575-128		9-252-66	9-251-51	9-119-45	9-34-9	9-138-33	9-35-11
	B(NJ)	14-18.5-3.5	12-440-139	e	12-156-47.4	12-191-63	12-89-30	12-134-78	12-259-111	12-32-7
	B(PA)	5-13.5-2.1	4-689-84		4-377-78	4-338-113	3-176-47	4-32-4	4-165-32	4-43-12
0414	A(NJ)	5-2.5-2	9-221-76	5-243-109	5-138-61	5-95-43	5-55-44	5-128-80	5-133-78	5-35-31
	A(PA)	4-4.5-0.6	7-199-75	4-420-109	4-332-75	4-267-24	4-288-29	4-60-28	4-73-45	4-75-18
0415	A(NJ)	7-6.5-3.6	f	e	7-167-71	7-163-70	7-162-70	7-88-25	7-102-36	7-18-6
	A(PA)	9-3.9-0.9	f	e	7-189-38	7-133-25	7-113-26	7-33-9	7-43-16	7-10-3
	B(NJ)	6-8.2-4.4	f	5-510-231	5-219-80	5-228-66	5-228-92	4-147-43	5-168-53	3-33-15
	B(PA)	4-4.1-1.0	f	3-547-21	3-296-38	3-187-15	3-154-18	2-62-20	3-60-13	2-17-8

[a] Rainfall volume in mm.
[b] From field pH.
[c] From laboratory pH.
[d] Samples were analyzed at PNL and BNL.
[e] Quality assurance pending.
[f] Analysis not performed.

"cycle" during light and intermittent precipitation. Figure 2 depicts the deposition of H^+ (from field pH) and NO_3^- for this storm. *B* values are generally higher than the corresponding *A* values; this can be attributed mostly to dry deposition between deployment and the onset of precipitation and between the cessation of precipitation and collection as well as the delayed response of the automatic collectors mentioned above. The deposition of most inorganic species showed general uniformity for this storm; the exceptions were Na^+ and Cl^- which showed higher values closer to the coast although they lacked the stratified pattern seen in the fall storms.[3] Table II presents the statistics of deposition for the various species. Although no control-target delineation was evident for this storm due to the veering transport, an artificial stratification between New Jersey and Pennsylvania stations was performed for comparison purposes. Table II also includes the statistics of deposition for the November and December 1983 storms (1111 and 1204) which were mentioned earlier.

Storm 0314

This storm was in some ways similar to 0306; it was associated with overrunning and started as snow. Approximately 1.2 cm of snow fell before changing to rain after a few hours. A difference from 0306 was the formation of a secondary low pressure system to the south of the network which slowly advanced northward. Based primarily on Atlantic City radiosonde data the main transport was easterly with a swing to northerly and northwesterly during the tail end of the storm. It can be assumed that the predominant upwind-downwind configuration was New Jersey-Pennsylvania. Figure 3 shows the secondary low and the collected deposition.

Amounts were generally greater than 0306 with heavier amounts in New Jersey. The deposition of nitrate and sulfate ions is shown in Figure 4. The excess target deposition of NO_3^- was ~45%, of $SO_4^=$ ~20%; excess deposition is defined as $100 \times (T - C)/C$ (%) where T and C are the spatial means of target and control deposition respectively (from Table II). The differences between *A* and *B* values are more pronounced for $SO_4^=$. There is some speculation that the high values of $SO_4^=$ at some southeastern sites may be associated with the plumes of two power plants on the New Jersey coast. Table II presents the statistics of deposition for all measured species. The ranges of some *A* concentration values were: for $SO_4^=$, 5.8–9.9 μmol/L in NJ and 7.5–16.1 μmol/L in PA; for NO_3^-, 3.2–5.0 μmol/L

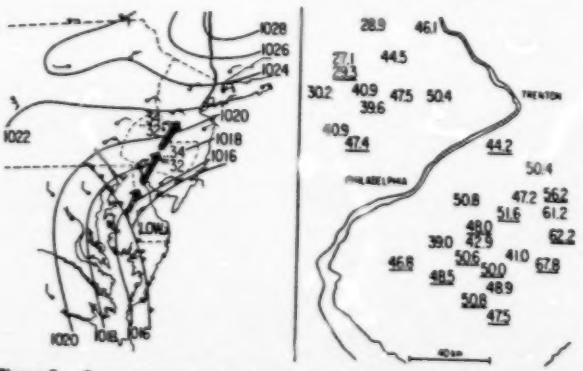

Figure 3. Storm 0314. Surface weather map for March 13, 1984, 2000 EST, showing the secondary low pressure system and its progress across the network. On the right are the rainfall amounts of 0314 (in mm). Underlined values represent *B* collectors.

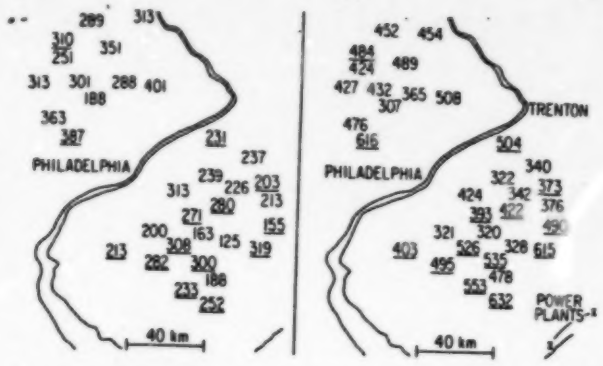

Figure 4. The deposition of NO_3^- (left) and $SO_4^=$ (right) for storm 0314 (March 13 and 14, 1984). The units are $\mu mol/m^2$. Underlined values depict *B* collectors. Also shown are the locations of two power plants along the New Jersey coast which may be responsible for some of the $SO_4^=$ at the southeastern sites.

in NJ and 4.6–10.4 μmol/L in PA. The ranges of field pH values were 4.72–4.91 in NJ and 4.53–4.81 in PA.

Storm 0405

Temperatures during this storm remained well above freezing and the precipitation from low stratus clouds was all rain. The storm was associated with overrunning an advancing warm front from the south; the low pressure system passed just west of the sampling area. Both surface and upper-level winds remained constant and southeasterly during the course of the precipitation and, consequently, a clear delineation of

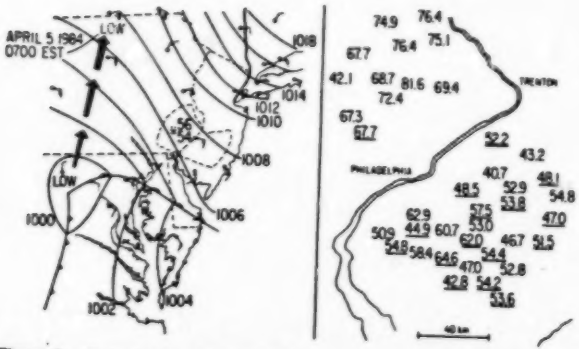

Figure 5. Storm 0405. Surface weather map for April 4, 1984, 2200 EST, showing the main low pressure system and its progression. The rainfall amounts (right), in mm, were the heaviest among the sampled storms.

control (NJ)-target (PA) areas was possible for this storm. The Atlantic City vertical wind profile (up to 7000 ft) showed very little directional change during the course of precipitation with only a moderate increase in wind speed. Figure 5 shows the surface weather map at 2200 EST and the collected rainfall amounts which were the heaviest among the storms of the sampling period. The rainfall distribution was generally uniform with heavier amounts in Pennsylvania. Figure 6 depicts the deposition of NO_3^- and NH_4^+. The increased, above background, deposition of NO_3^- is ~200%, a clear indication of an effect of emissions from the Delaware River Valley. What is perhaps more striking is the gradual increase in the deposition with distance from the valley suggesting that the zone of maximum impact may be beyond the 60 km radius representing the boundary of the network. The New Jersey-Pennsylvania contrast for $SO_4^=$ was not as large (40%). The deposition of NH_4^+ showed an increase of ~80% with quite uniform amounts in New Jersey. The uniformity of NH_4^+ deposition is considered surprising as NH_4^+ is usually affected by extremely local sources.[5] For this storm the deployment and collection of the *B* samplers coincided fairly well with the onset and cessation of precipitation and, consequently, the differences between *A* and *B* values were small. For this storm chemical analyses of the rain samples were performed at both BNL and PNL for QA purposes. Table II includes the results from both laboratories. The ranges of some *A* concentrations based on BNL laboratory results were: for $SO_4^=$, 14.0–20.7 μmol/L in NJ and 14.7–27.2 μmol/L in PA; for NO_3^-, 4.9–7.2 μmol/L in NJ and 7.9–24.5 μmol/L in PA; for NH_4^+, 5.9–8.8 μmol/L in NJ and 6.4–15.7 μmol/L in PA. The ranges of field pH values were 4.49–4.61 in NJ and 4.26–4.57 in PA.

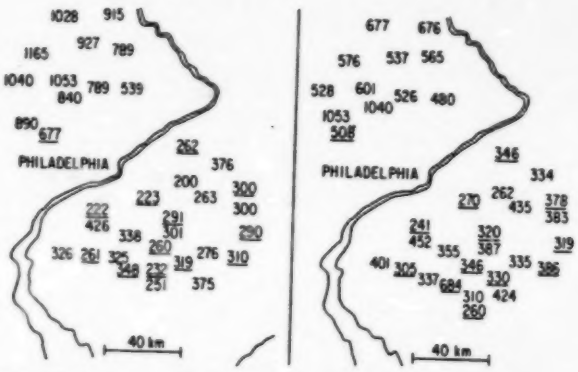

Figure 6. The deposition of NO_3^- (left) and NH_4^+ (right) for storm 0405 (April 4 and 5, 1984). The units of deposition are $\mu mol/m^2$ and *B* values are underlined.

Storm 0424

This storm was remarkably similar to the two fall 1983 sampled storms. Following the dissipation of a west-east warm front, a secondary low pressure system developed in eastern Virginia and tracked to the northeast passing just east of the network. Surface winds remained easterly during the course of precipitation while the 850 mb winds were mostly southerly. This contributed to an overall southeasterly transport and permitted another clear control (NJ)-target (PA) delineation. Figure 7 shows the surface weather map for 1300 EST of April 23 and the rainfall amounts. Precipitation was all rain with steady rainfall rates; amounts were heavier at the southern portion of the network. Figure 8 shows the deposition of NO_3^-

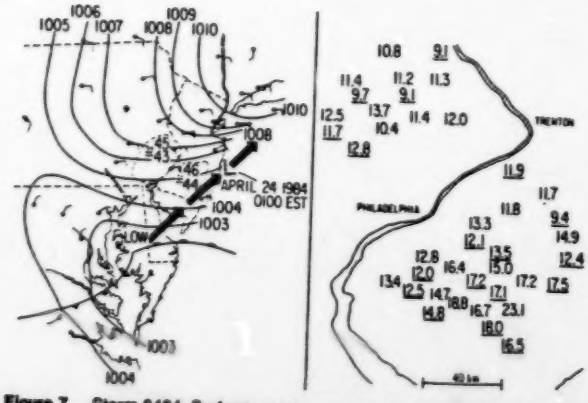

Figure 7. Storm 0424. Surface weather map for April 23, 1984, 1300 EST, showing the secondary low pressure system and its progression. Rainfall amounts (right) of 0424 are in mm.

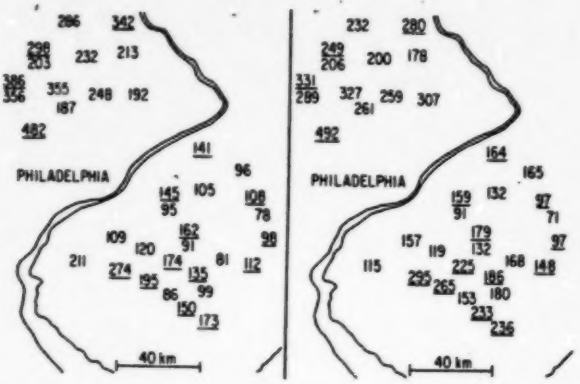

Figure 8. The deposition of NO_3^- (left) and $SO_4^=$ (right) for storm 0424 (April 22 and 23, 1984) in $\mu mol/m^2$. *B* values are underlined.

and $SO_4^=$. Delaware Valley emissions appear to have impacted both species; the increased target deposition of NO_3^- was ~140%, for $SO_4^=$ ~90%. Some of the high values along the southwestern edge of the network may again be associated with the plumes of the two power plants along the New Jersey shore. Once again, the outward increase in the deposition of NO_3^- suggests a larger than 60 km zone of impact of the Valley emissions. The *A*-*B* differences were among the highest of the sampled storms. This reflects both a less than ideal timing of deployment and collection of the *B* samplers as well as the possibility that increased agricultural and biological activity associated with moderating temperatures leads to increased dryfall contamination. Table II presents the statistics of deposition for the various ionic species. The ranges of some of the *A* concentrations were: for $SO_4^=$, 4.5–15.6 μmol/L in NJ and 15.7–32.9 μmol/L in PA; for NO_3^-, 4.9–14.3 μmol/L in NJ and 25.4–28.9 μmol/L in PA; for NH_4^+, 3.2–8.9 μmol/L in NJ and 10.0–18.6 μmol/L in PA. The ranges of the field pH values were 4.44–4.88 in NJ and 4.22–4.43 in PA.

Storms 0414 and 0415

These two weekend storms are examples of less than ideal situations for sampling purposes. They are, however, typical of a large portion of wet deposition events and are presented to highlight the inherent difficulties of obtaining reliable longer-term estimates of wet deposition from event-type sampling. Both storms were associated with a deep low pressure system which moved slowly across northern Illinois and Indiana. Two successive west-east weak warm fronts associated with this low influenced the weather over the network, the first crossing the network during the first event (0414), the second remaining to the south during the second event (0415). The lack of a clear organization for this storm contributed to erroneous forecasts and somewhat compromised sampling operations. The same system contributed to a series of mostly scattered showers during the early part of the week of April 16 that were not sampled.

Storm 0414 was characterized by two 3-h periods of light rain around 1500 EST of April 13 (first warm front passage) and 0000 EST of April 14. Only the *A* network was activated and only nine sites produced enough sample for complete analyses. Surface winds were southeasterly to northeasterly during this period with upper winds veering from southerly to easterly during the same time; transport was determined as mostly southeasterly. Target deposition of NO_3^-, $SO_4^=$, and NH_4^+ were higher than control deposition but the low rainfall volumes and the isolated showers during the retrieval process compromise this result.

During the retrieval of the 0414 samples both *A* and *B* networks were activated in anticipation of a forecasted more substantial precipitation event which did not materialize. Instead, only a period of light but steady rain occurred during the early morning hours of April 15. During the retrieval of the 0415 samples in the late morning a series of thunderstorms developed at the southeastern part of the network. The samples affected by these showers were not considered part of this storm.

Discussion

In the quest for a quantitative assessment of the influence of urban and industrial emissions on mesoscale acid deposition, the Philadelphia field study results should prove quite useful. Some of the conclusions of the exploratory phase are strengthened, particularly with regard to the impact of fresh emissions on the production and deposition of nitric acid. If synoptic transport over the lowest kilometers of the atmosphere remains steady during the storm and the control-target distinction can be confidently made, target deposition of nitrate may increase by as much as 200%. This was the case for Storm 0405 and the November 1983 storm (1111) which registered the highest target-control increase both in absolute and relative terms. The increase for 0424 was somewhat less (~140%), while for 0314 the veering transport during the tail end of the storm may have diluted the final impact (~50%). It should be noted that for those storms which registered an effect the target-control contrast would have been more dramatic if concentration rather than deposition values were used; the only exception was Storm 0405 which was the only one among those storms with greater rainfall volumes over Pennsylvania. For 1111 the average nitrate concentrations were 5.9 μmol/L in New Jersey and 32.8 μmol/L in Pennsylvania. Veering transport is considered responsible for the uniform pattern of 0306 while for 0414 and 0415 no firm conclusions can be reached because of less than ideal sampling circumstances and insufficient rainfall amounts. Large differences between control-target rainfall amounts have also compromised storms 0321 and 0326, while the catastrophic features of 0329 created QA problems. It is important to emphasize the difficulties of using event-type sampling to estimate longer-term (seasonal or annual) differences and trends since a considerable fraction of total wet deposition may be associated with less organized weather systems causing long, intermittent, and spatially inhomogeneous rain events. Nevertheless, it is felt that only event-type sampling and perhaps sequential within-event sampling can provide the comprehensive information blocks required to determine the impact of local sources. Such information blocks, together with a firm knowledge of precipitation climatology, may provide the necessary assessments of impact on longer time scales. The importance of event-type sampling is highlighted with the

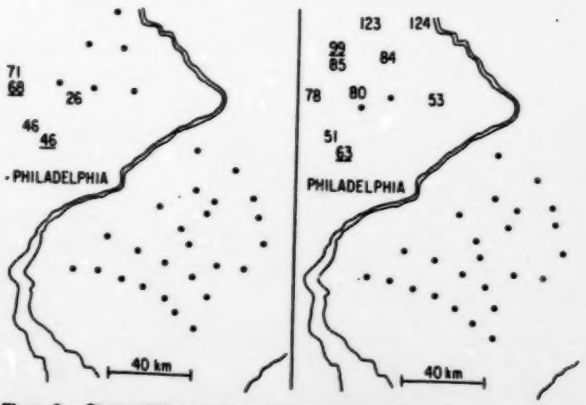

Figure 9. Storms 0306 and 0314. The deposition of dissolved SO_2 (in $\mu mol/m^2$) for storms 0306 (left) and 0314 (right). Dots denote values below the detection limit of 1 μmol/L concentration.

Table III. Maximum-minimum temperatures (°F) for various locations in and around the sampling network during the storms.

Storm	Dates	Wilmington (DE)	Philadelphia (PA)	Phoenixville (PA)	Atlantic City (NJ)
1111	11/10/83	61–41	57–44	58–35	62–42
	11/11/83	61–37	60–39	61–45	62–37
1204	12/4/83	48–35	47–35	43–31	51–36
0306	3/5/84	40–31	41–29	36–29	51–32
	3/6/84	43–35	43–35	44–34	55–39
0314	3/13/84	37–23	35–23	35–22	53–28
0321	3/21/84	61–41	60–39	60–38	56–46
0326	3/25/84	44–37	43–36	46–36	44–37
0329	3/27/84	50–30	52–30	54–36	49–28
	3/28/84	41–37	40–36	55–28	41–37
	3/29/84	39–34	37–33	37–33	39–33
0405	4/4/84	58–44	56–44	57–41	54–43
	4/5/84	65–47	66–48	64–48	58–45
0414	4/13/84	67–46	68–42	67–45	60–46
	4/14/84	51–44	49–44	55–44	51–44
0415	4/15/84	52–44	50–43	48–45	51–44
0424	4/22/84	50–32	49–36	61–32	47–33
	4/23/84	49–36	47–36	47–36	53–37

December 1983 storm (1204) which contrasted the majority of the sampled storms. This storm showed only an excess in the deposition of dissolved sulfur dioxide despite its meteorological and transport similarities with the others. Three possible explanations have been proposed,[6] the leading one attributing the observed pattern to the reduced concentrations of oxidants (OH below cloud and H_2O_2 in cloud) due to the nighttime occurrence of the precipitation. The second explanation was based on an emissions-modulation hypothesis since the December 1983 storm occurred on an early Sunday morning which represents the period of lowest transportation and manufacturing emissions.[3] Another possible explanation may be based on the subtle meteorological circumstances which may have, for example, suppressed the required incorporation of fresh emissions or oxidants into the cloud layer. It is also possible that the December 1983 storm results may be the product of a synergistic contribution from all three explanations. None of the storms of the March-April experimental period exhibited the exclusive characteristics of the December storm and, consequently, no further experimental support of an individual explanation can presently be pursued. At the same time, the exclusive nature of this storm may, from a statistical standpoint, deemphasize its importance in estimating longer-term assessments of local source contributions. As will be discussed later, future plans include both a continuation of the field efforts and a comprehensive modeling exercise to address, among others, the relative importance of the above explanations.

The impact of the urban and industrial emissions on the deposition of $SO_4^=$ appears less striking compared to the deposition of NO_3^-. The maximum target-control increase was seen for storm 0424 which showed a ~90% rise. Among the others that showed an increase it averaged about 30%. The December storm exhibited a 240% increase in the deposition of dissolved SO_2; the presence of these unreacted SO_2 amounts in the rain is another indication of the exhaustion of H_2O_2 in cloudwater[20] which reduces the extent of SO_2 oxidation. Among the storms of the March-April period, only 0306 and 0314 showed some dissolved SO_2 (Figure 9). Particularly for 0314, the presence of substantial amounts of unreacted SO_2 in the target area may be another indication of reduced oxidant availability contributing to lower increases in the deposition of both $SO_4^=$ and NO_3^-, although the veering transport during the precipitation most certainly contributed to the dilution. Reference has been made to possible meteorological differences between storms, contributing to the observed differences in deposition. Table III presents the maximum-minimum daily temperatures for various locations in and around the network during the sampled storms. The apparent temperature dependence of dissolved SO_2 is in line with the published literature[21,22] on the seasonal dependence of dissolved SO_2 in rainwater.

As mentioned earlier, there is some speculation that the two power plants close to Atlantic City on the New Jersey coast may be responsible for the observed high values of $SO_4^=$ deposition at some southeastern sites of the network. There is considerable interest in determining the contribution of primary $SO_4^=$ emissions to the target-control $SO_4^=$ excess, particularly with regard to the residential heating emissions. Based on the available data, and particularly the absence of or small size of target-control contrast of $SO_4^=$ when dissolved SO_2 values are significant, primary $SO_4^=$ emissions may be considered unimportant. Therefore, it is reasonable to conclude that the observed $SO_4^=$ excess is mostly the result of rapid SO_2 to $SO_4^=$ oxidation, particularly in the liquid phase.

The more substantial impact of the valley emissions on NO_3^- rather than $SO_4^=$ can be rationalized on several grounds. First, based on current experimental and theoretical knowledge, there exist more pathways with faster overall rates for the conversion of NO_x to HNO_3 compared to the SO_2 to H_2SO_4 rates in the gas phase[23–25]; although the reverse is true for the aqueous phase,[26] the availability of H_2O_2 may be the deciding rate limiting factor. Furthermore, gaseous nitric acid is removed from the atmosphere much more rapidly than particulate sulfate, and some fine particle nitrates can volatilize to release nitric acid.[27] Second, both the quantity and nature of NO_x vs. SO_x emissions may promote a more vigorous HNO_3 production. This may be related to the more diffuse and lower-level manufacturing industry, refinery, and transportation emissions of NO_x compared to the emissions of SO_2, which may be dominated by a few higher-level sources. The diffuse nature of the NO_x emissions may provide longer residence times, more efficient mixing with other pollutants and oxidants[28] and generally greater availability for reaction and scavenging both in-cloud and below-cloud.

An attempt was made to estimate the relationship between the deposited excess NO_3^- and $SO_4^=$ for the various storms and the emitted NO_x and SO_x in the sampling region. The development of a detailed emissions inventory for the entire eastern United States is an important objective of NAPAP.[29] The estimates presented here are based on existing emissions inventories.[30] According to the estimates, ~80% of all SO_x and NO_x emissions in the sampling area occur within 20 km of the Delaware River. Table IV presents those estimates for both areal and point sources. Assuming uniform emission rates

Table IV. Estimates of NO_x and SO_x emission rates (in tons/year) along the Delaware Valley.

	NO_x	SO_x
Point sources	110,000	170,000
Areal sources	140,000	40,000
Total	250,000	210,000

(from Table IV) and taking into consideration the periods of rainfall, the ratio of deposited excess NO_3^- in the downwind sector to emitted NO_x is estimated to be ~50% for the November storm, ~30% for 0405 and less than 10% for 0424 and 0314. For the corresponding sulfur (dissolved SO_2 and $SO_4^=$) estimates, we have ~20% for the November, December, and 0405 storms, and less than 10% for 0424 and 0314.

Storm 0424 showed a sizable target-control relative increase but a low excess deposition to emission ratio for both nitrogen and sulfur. Apart from the strong meteorological and transport similarities with the December 1983 storm there was some similarity with the time of occurrence as well. A considerable fraction of the 0424 rain occurred over a Sunday (in fact the Easter Sunday) to Monday evening and consequently some emissions (primarily manufacturing and transportation) may have been reduced during the early part of the storm compared with the average weekday values leading to the low excess deposition-to-emission ratios. Nevertheless, the sizable target-control relative increases of NO_3^- and $SO_4^=$ indicate that the similarities with the December storm did not extend to the suppression of HNO_3 and H_2SO_4 production.

It is important to emphasize that for those cases with an increased target deposition of NO_3^-, the effect appears to increase with distance from the Delaware Valley, suggesting perhaps that the impact may indeed peak beyond the distance of 60 km which represents the domain of the sampling network. This suggestion may have important implications regarding the estimates of deposition to emission ratios presented above. Assuming a peak at 80 km and extrapolating the deposition estimates to 100 km downwind of the Valley, almost 100% of the emitted NO_x may be transformed and deposited as nitric acid on the mesoscale. It should be pointed out that the above mentioned 100% transformation rate may occur only during the precipitation periods and, consequently, for long-term estimates which include both wet and dry periods, the importance of local contributions to the total acid deposition may be deemphasized.

The observed patterns of NH_4^+ deposition is one of the surprises of the field results. It has generally been assumed that the distribution of NH_4^+ is spotty,[5] perhaps as the consequence of local ammonia sources. In fact, for most of the sampled storms, the coefficient of spatial variation of NH_4^+ is comparable to the ones for the other species. Furthermore, this ion registered a ~100% increase in target deposition for storm 0424 and a ~70% increase for the November and 0405 storms thus implicating the urban and industrial emissions. The processes responsible for this result are the subject of continuing studies.

With one exception, the deposition of Na^+ mirrors the deposition of Cl^-. This is expected from the proximity of the sampling network to the coast and the predominance of sea salt as the source of Na^+ and Cl^-. The stratified patterns of Na^+ and Cl^- deposition with the monotonic decrease with distance from the coast were another confirmation of the southeasterly transport which dominated the sampled events. Even the slight excess of Cl^- is in agreement with results from the MAP3S/RAINE precipitation chemistry network.[31] The exception is Storm 0424 which showed considerably higher Cl^- to Na^+ ratios over the entire network. The cause for this exception is as yet undetermined.

A return to the field is planned for the spring of 1985. The planned field experiment will be a joint endeavor of the "Mesoscale" and PRECP[32] Programs. The network will be extended toward the northwest (to the cities of Reading, Allentown, and Bethlehem) in order to determine the zone of maximum impact which eluded the recent experimental efforts; it is assumed that the predominant transport during the sampled storms will remain southeasterly. Two additional sampling dimensions are planned to enhance the understanding of the relevant atmospheric chemical processes: airborne measurements using BNL's Beechcraft Queen Air aircraft and sequential ground level sampling.[33] The airborne measurements will include NO_x, HNO_3, aerosols, SO_2, and H_2O_2 and will cover both spirals for vertical distributions and crosswind traverses (in cloud and below cloud) in the target and control areas. The sequential sampling is expected to maximize the value of collected data by providing insights into the within storm variability of changing emissions, oxidants, and potential transport.

A modeling activity is currently underway which is expected to address the existing (past and recent) and planned field data. This activity will complement the development of the Regional Acid Deposition Model (RADM) at the National Center for Atmospheric Research[34] by concentrating on the mesoscale, thus assisting in the characterization of the subgrid parameterizations. Preliminary efforts will concentrate on identifying the processes (both meteorological and chemical) which produce the field results using a diagnostic Lagrangian model[35] with lumped emissions inputs and meteorological parameterizations. These efforts will be the prelude to the mesoscale Eulerian model which will combine a dynamic model[36] and a transport-chemical model.[37]

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